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(54) Title: DENTAL ALLOY WITH SILVER CONTENT

(57) Abstract: Alloys composed of 35.5 to 62.5 % silver, 4.1 to 11.0 % indium, 5 to 37.0 % gold, 0 to 40.0 % platinum, 0 to 35 % palladium, 0 to 9.5 % zinc, tin, gallium, copper, 0 to 2.0 % iridium, rhenium, rhodium, ruthenium, 0 to 5.0 % boron, cobalt, chromium, iron, germanium, niobium, nickel, silicon, tantalum, titanium, manganese, vanadium, the indicated percentages being percentages by weight. On one hand, such alloys are inexpensive, and on the other hand, their physical properties with respect to the coefficient of thermal expansion make them suitable for veneering. Furthermore, they show a desired yellowish colour and improved corrosion resistance and mechanical properties.

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Dental Alloy With Silver Content

The present invention refers to a dental alloy with silver content according to the preamble of claim 1.

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A large number of such silver alloys are known, which are mainly used because they are less expensive than high gold alloys. The different silver alloys are adapted to different kinds of indications. In these alloys, an elevated palladium
10 content is required to compensate for the high thermal expansion coefficient of silver if they are to be veneered by ceramic material.

As an alternative, alloys of high gold content have been
15 veneered by ceramics.

Gold alloys show a desired yellow appearance, yet have a low melting point not well suited to veneering by ceramics as the material is loosing its shape while the ceramic material
20 is fused to the alloy body. The gold or gold alloys also have a relatively high density, hence more of the rather expensive material is needed.

Regarding silver palladium alloy, a superficial oxide layer
25 is necessary to secure the fast adherence of the ceramic material on the silver palladium alloys. This oxide layer is produced by a particular oxide firing step and shows a rather dark colour which would impair the optical appearance of the veneered area. Even if special opaque layers of
30 ceramic are applied, the dark colour is perceivable in the boundary areas where the ceramic layer is thin, and of course at the periphery of the ceramic veneer. In order to avoid this effect, the surface may be specially treated so that the oxide gets a light or nearly white colour, yet this
35 treatment again increases the overall costs and does avoid

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that the product shows an unnatural appearance resembling steel.

Other drawbacks of silver palladium alloys are that delicate
5 structures are difficult to be casted in comparison with gold,
and the neutral, metallic appearance where the surface of
the alloy is visible, i.e. at the non-veneered surface
areas.

10 Regarding the incorporation of palladium, not only
contravenes the use of this expensive noble metal the goal
to provide a non-expensive alloy, it renders its price also
prone to large changes due to the highly volatile market of
the platinum metals.

15 Another aspect is the availability of ceramics which can be
fused to an alloy body using lower firing temperatures.
These ceramics, however, show also a higher thermal
expansion, generally higher than $14.5 \cdot 10^{-6} \text{ K}^{-1}$. For a
20 stable and rigid bond among ceramic and alloy, the thermal
expansion of alloy and ceramic has to be matched, the
thermal expansion of the ceramic preferably being slightly
less than that of the alloy, e.g. by about 1 K^{-1} or less.

25 JP-A-2001 192 170 proposes an alloy based mainly on silver,
palladium and gold. The proposed total contents of copper
and zinc according to the embodiments is at least 11 %, and
the alloys have thermal expansion coefficients of at least
 $18 \cdot 10^{-6} \text{ K}^{-1}$. It is not mentioned that ceramics are capable
30 to be fused to a body of the these alloys, but additionally
to dentistry, their use is extended to repairing decorative
parts, electrical contacts etc. Finally, the high thermal
expansion of the exemplary alloys forbids the use for
ceramic-fused-to-metal dental devices.

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- NL-A-9 200 566 relates to a dental alloy, on which ceramics may be fused. The lowest melting range of the embodiments given is 990-1110 °C, and the thermal expansion coefficients of the embodiments are $(15.5 \text{ to } 17.5) \times 10^{-6} \text{ K}^{-1}$. The
- 5 compositions of the embodiments of the alloy with respect to silver, palladium and indium is characterized by the values (Ag/Pd/In, weight percentages): 43/44/8.5; 68.2/22/6.5; 49.5/40/7.5. Gold is contained at most by 1 %.
- 10 EP-A-0 178 506 proposes similar silver palladium alloys showing a solidus temperature of 1075 °C or more. One characteristic feature of these alloys is the content of at most 0.5 % gold or the absence of gold.
- 15 DE-A-197 13 925 discloses silver palladium alloys with at most 1 % gold. The alloys show solidus temperatures of at least 1015 °C.

- Else, the alloys according to the three aforementioned
- 20 publications show the general drawbacks for silver palladium alloy as set forth above.

- Therefore, it is desirable and thus also an object of the invention to provide a dental alloy with silver content that
- 25 is suitable for a large number of applications ranging from inlays to long-span bridgework and offers improved mechanical properties, particularly a higher stability and corrosion resistance, and is compatible with low fusing ceramics with high thermal expansion coefficient, i.e.
- 30 suitable for veneering. Furthermore, the alloy shall have a yellow colour, i. e. resemble gold.

This object is attained by the alloy according to claim 1.
If the dental alloy is to meet very high requirements with

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respect to mechanical stability, the dental alloy according to claim 2 is preferred.

The other claims define preferred embodiments of the alloys
5 and uses thereof and products obtained.

Detailed Description of the Invention

The invention will be explained in more detail hereinafter
10 with reference to exemplary embodiments. As illustrated by the silver dental alloys of the prior art, and as it is known to those skilled in the art from tests, books and the like, certain elements besides the noble metal components will provide certain effects, and it is known that e.g. zinc
15 will harden an alloy, or iridium may be used as a grain refiner. The same applies to additional metals such as rhodium, ruthenium and the like.

Within the whole specification including the claims,
20 percentages are by weight.

Surprisingly, extensive tests have now shown that the alloy described hereinafter, by the mere addition of palladium and indium to an alloy containing silver and gold within the
25 indicated limits, provides a high corrosion resistance, improved mechanical properties and a coefficient of thermal expansion that makes it suitable for veneering particularly by low-fusing ceramics having a coefficient of thermal expansion ranging from 14.5 to 16.5. Furthermore, the alloy
30 has ameliorated casting properties so that delicate surface structures can be mold without difficulty. Subsequent grinding and polishing for the finish of the cast object and elaborating minute details can be readily done without applying undue force. Still to mention that the alloy shows
35 a yellowish colour, which is preferred for esthetical

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reasons. Ceramic material may be fused to the alloy directly, the problem with the dark coloured oxide surface layer does not arise.

- 5 The alloy is composed of 35.5 to 62.5 % silver, 4.1 to 11.0 % indium, 5 to 37.0 % gold, 0 to 40.0 % platinum, 0 to 35 % palladium, 0 to 9.5 % zinc, tin, gallium, copper, 0 to 2.0 % iridium, rhenium, rhodium, ruthenium, 0 to 5.0 % boron, cobalt, chromium, iron, germanium, niobium, nickel, silicon,
10 tantalum, titanium, manganese, vanadium, the indicated percentages being percentages by weight.

- Within the indicated limits, test series have shown that a suitable dental alloy having an increased stability is
15 composed of 38.0 to 62.0 % silver, 4.5 to 11.0 % indium, 5 to 35.0 % gold, 0 to 20.0 % platinum, 8.0 to 35.0 % palladium, 0 to 7.0 % zinc, tin, gallium, copper, 0 to 2.0 % iridium, rhenium, rhodium, ruthenium, boron, cobalt, chromium, iron, germanium, niobium, nickel, silicon,
20 tantalum, titanium, manganese, vanadium.

- Further useful alloys are composed of 40.0 to 62.0 % silver, 5.0 to 10.0 % indium, 5 to 33.0 % gold, 0 to 15.0 % platinum, 10.0 to 32.0 % palladium, 0 to 7.0 % zinc, tin,
25 gallium, copper, 0 to 2.0 % iridium, rhenium, rhodium, ruthenium, boron, cobalt, chromium, iron, germanium, niobium, nickel, silicon, tantalum, titanium, manganese, vanadium.

- 30 A further alloy may have the following composition: 45.0 to 62.0 % silver, 5.0 to 10.0 % indium, 5 to 20.0 % gold, 0 to 15.0 % platinum, 20.0 to 35.0 % palladium, 0 to 7.0 % zinc, tin, gallium, copper, 0 to 2.0 % iridium, rhenium, rhodium, ruthenium, boron, cobalt, chromium, iron, germanium,

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niobium, nickel, silicon, tantalum, titanium, manganese,
vanadium.

A preferred alloy with gold content and having an esthetic
5 yellow color is composed of 38.0 to 55.0 % silver, 5.0 to
10.0 % indium, 20.0 to 35.0 % gold, 0 to 15.0 % platinum,
8.0 to 20.0 % palladium, 0 to 7.0 % zinc, tin, gallium,
copper, 0 to 2.0 % iridium, rhenium, rhodium, ruthenium,
boron, cobalt, chromium, iron, germanium, niobium, nickel,
10 silicon, tantalum, titanium, manganese, vanadium.

The gold content improves the corrosion resistance, hence
counteracts the tendency of increased corrosion caused by
the lower content of palladium as well as by the presence of
15 indium and palladium in combination. On the other hand,
gold, palladium and indium together yield a desirable
increase in hardness.

Copper may also be present in an amount of at most 0.5 %, or
20 be totally absent.

The composition and characteristic physical properties of
exemplary alloys according to the invention are shown in the
Tables 1 and 2 below.

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Alloy	I	II	III	IV	V
Component	Fraction	Fraction	Fraction	Fraction	Fraction
	%	%	%	%	%
Silver	42	42	45	45	42
Gold	32	32	32	32	32
Palladium	14.98	15	14.8	14.8	14.8
Indium	9	9	5		9
Platin	2	2	2	2	2
Ruthenium	0.02		0.2	0.2	0.2
Gallium			1		
Boron					
Tin				6	

Table 1

Physical Property	Alloy I	Alloy II	Unit
Melting interval	990-1070	990-1070	°C
Density	12.7	12.7	g/cm ³
Elasticity module	100	100	GPa
Thermal expansion (25-500 °C)	17*10 ⁻⁶	17*10 ⁻⁶	K ⁻¹
Colour	pale yellow	pale yellow	
Hardness HV ₅ after cast	190	190	
Elongation A5	6.9	4.5	%
Corrosion: Re-lease of ions (ISO 10271)	1.34	3.6	10 ⁻⁶ g/cm ² during 7 days

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Physical Property	Alloy III	Alloy IV	Alloy V	Unit
Melting interval	995 - 1080	1015-1060	990-1075	°C
Thermal expansion (25-500 °C)	$17.2 \cdot 10^{-6}$	$16.9 \cdot 10^{-6}$	$16.9 \cdot 10^{-6}$	K ⁻¹
Colour	pale yellow	pale yellow	pale yellow	

Table 2

In summary, it will be noted that the suggested alloys

- a) correspond to the ISO 9693:1999 and ISO 8891:1998 standards, i.e. that they are both dental casting alloys and restorative metal-ceramic alloys suitable for veneering mainly but not exclusively with low-fusing ceramics having a high coefficient of thermal expansion,
- b) offer very good mechanical properties, particularly a high stability, even after the firing of low-fusing, highly expanding ceramic substances;
- c) a high firing stability in the firing cycles of the ceramic materials;
- d) a very high corrosion and tarnishing resistance in spite of the high silver content;
- e) are capable of fulfilling high esthetic requirements;
- f) particularly in view of the incorporation of indium, surprisingly, it has been found that the alloys do not show the susceptibility to corrosion as experienced with low price alloys of the silver palladium type with reduced gold and high indium content which had been marketed in the 1980's.

From the description and the exemplary embodiments, the one skilled in the art is enabled to derive variations of the

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invention without leaving the scope of protection which is defined by the claims.

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Claims

1. Ceramics-fused-to-metal dental alloy with silver content, composed of 35.5 to 62.5 % silver, 4.1 to 11.0 %
5 indium, 5.0 to 37.0 % gold, 0 to 40.0 % platinum, 0.0 to 35.0 % palladium, totally 0 to 9.5 % zinc, tin, gallium, and/or copper, totally 0 to 2.0 % iridium, rhenium, rhodium, and/or ruthenium, totally 0 to 5.0 % boron, cobalt, chromium, iron, germanium, niobium, nickel, silicon,
10 tantalum, titanium, manganese, and/or vanadium, the indicated percentages being percentages by weight.
2. The dental alloy of claim 1, composed of 38.0 to 62.0 % silver, 4.5 to 11.0 % indium, 5 to 35.0 % gold, 0 to 20.0 %
15 platinum, 8.0 to 35.0 % palladium, totally 0 to 7.0 % zinc, tin, gallium, and/or copper, totally 0 to 2.0 % iridium, rhenium, rhodium, ruthenium, boron, cobalt, chromium, iron, germanium, niobium, nickel, silicon, tantalum, titanium, manganese, and/or vanadium, the indicated percentages being
20 percentages by weight.
3. The dental alloy of claim 1, composed of 40.0 to 62.0 % silver, 5.0 to 10.0 % indium, 5 to 33.0 % gold, 0 to 15.0 % platinum, 10.0 to 32.0 % palladium, totally 0 to 7.0 %
25 zinc, tin, gallium, and/or copper, totally 0 to 2.0 % iridium, rhenium, rhodium, ruthenium, boron, cobalt, chromium, iron, germanium, niobium, nickel, silicon, tantalum, titanium, manganese, and/or vanadium.
- 30 4. The dental alloy of claim 1, composed of 45.0 to 62.0 % silver, 5.0 to 10.0 % indium, 5 to 20.0 % gold, 0 to 15.0 % platinum, 20.0 to 35.0 % palladium, totally 0 to 7.0 % zinc, tin, gallium, and/or copper, totally 0 to 2.0 % iridium, rhenium, rhodium, ruthenium, boron, cobalt,

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chromium, iron, germanium, niobium, nickel, silicon,
tantalum, titanium, manganese, and/or vanadium.

5. The alloy of one of claims 1 to 4, wherein the gold
5 content is at least 10 %.

6. The alloy of claim 5, wherein the gold contents is at
least 20 %.

10 7. The dental alloy of claim 1, composed of 38.0 to
55.0 % silver, 5.0 to 10.0 % indium, 20.0 to 35.0 % gold, 0
to 15.0 % platinum, 8.0 to 20.0 % palladium, totally 0 to
7.0 % zinc, tin, gallium, and/or copper, totally 0 to 2.0 %
15 iridium, rhenium, rhodium, ruthenium, boron, cobalt,
chromium, iron, germanium, niobium, nickel, silicon,
tantalum, titanium, manganese and/or vanadium.

8. The alloy of one of claims 1 to 7, wherein manganese is
absent.

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9. The alloy of one of claims 1 to 8, wherein the content of
copper is at most 0.5 % and preferably copper is absent.

10. Use of the alloy of one of claims 1 to 9 for producing
25 dental prosthetic parts, wherein a layer of ceramic material
is fused to a body essentially consisting of the alloy.

11. Use of the alloy according to claim 10, wherein the
ceramic material has a thermal expansion coefficient of at
30 least $14.5 \times 10^{-6} \text{ K}^{-1}$, preferably within the range of $(14.5$
to $16.5) \times 10^{-6} \text{ K}^{-1}$.

12. A dental prosthetic part obtained according to claim 10
or 11.

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INTERNATIONAL SEARCH REPORT

In tional Application No

PCT/CH 02/00539

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K6/04 C22C5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 10, 17 November 2000 (2000-11-17) & JP 2000 192170 A (NIPPON SHIKEN KOGYO KK), 11 July 2000 (2000-07-11) abstract ---	1-10
X	DATABASE WPI Section Ch, Week 199345 Derwent Publications Ltd., London, GB; Class D21, AN 1993-357962 XP002186571 -& NL 9 200 566 A (ELEPHANT EDELMETAAL BV) , 18 October 1993 (1993-10-18) abstract --- -/--	1-12

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/CH 02/00539

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 178 506 A (DEGUSSA) 23 April 1986 (1986-04-23) page 2, line 30 -page 3, line 20 claims; table ---	1-4,8
X	DE 197 13 925 C (DEGUSSA) 29 October 1998 (1998-10-29) page 2, line 64 -page 3, line 46 claims; tables ---	1-4,8
A	US 5 462 437 A (PRASAD ARUN ET AL) 31 October 1995 (1995-10-31) column 3, line 8 - line 20 column 3, line 29 - line 36 column 4, line 7 - line 38 claims ---	1-12
A	US 5 290 371 A (CAMERON THOMAS B ET AL) 1 March 1994 (1994-03-01) column 2, line 16 - line 51 claims -----	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CH 02/00539

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 2000192170	A	11-07-2000	NONE	
NL 9200566	A	18-10-1993	NONE	
EP 0178506	A	23-04-1986	DE 3438288 C1 AT 55242 T CA 1254771 A1 DE 3579096 D1 EP 0178506 A2	04-07-1985 15-08-1990 30-05-1989 13-09-1990 23-04-1986
DE 19713925	C	29-10-1998	DE 19713925 C1 BR 9809747 A WO 9844894 A2 EP 0973480 A2 JP 2001518812 T US 6290501 B1	29-10-1998 20-06-2000 15-10-1998 26-01-2000 16-10-2001 18-09-2001
US 5462437	A	31-10-1995	NONE	
US 5290371	A	01-03-1994	NONE	